Functional Hyperbranched Polymers Using Ring-Opening Metathesis Polymerization of Dicyclopentadiene with Monoterpenes

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ABSTRACT: A general method for the synthesis of hyperbranched functional polymers in monoterpenes is described. During the polymerization of dicyclopentadiene, metathesis reactions between the growing polymer chain and monoterpenes produced soluble well-defined polymers. The molecular weight, intrinsic viscosity [η], and glass transition temperature (T_g) values resulting from chain transfer to monoterpenes depended on the mode of monomer addition but generally decreased as follows: *d*-limonene > limonene oxide > β-pinene. Calculation of the Mark–Houwink–Sakarada values by gel permeation chromatography suggested that, in solution, the branched poly(dicyclopentadiene) had a smaller hydrodynamic volume than polynorbornene. Characterization by NMR spectroscopy indicated the hyperbranched polymer had a complex structure composed of linear, terminal, semidendritic, and dendritic units.

Introduction

The topology of hyperbranched polymers varies widely with polymerization mechanism, monomer functionality, and experimental parameters.[1–3] Since a large number of terminal units on hyperbranched polymers strongly impact the solution and bulk properties relative to their linear analogues,[4] the ability to control branching, molecular weight, and chemical functionalities is an important and challenging synthetic task. Ring-opening mechanisms have become prevalent methods to produce hyperbranched polycarbonates,[5] polyethers,[6,7] polyesters,[8] polylactides,[9] and poly(ether amides).[10] Although ring-opening metathesis polymerization (ROMP) of cyclic alkenes has not been reported for homogeneous hyperbranched polymers, metathesis reactions provide access to diverse chemical functionalities and polymer architectures via intramolecular metathesis cross-linking reactions,[11,12] acyclic diene metathesis (ADMET) polymerizations,[13,14] cross-metathesis reactions,[15,16] and chain transfer.[17]

Chain transfer during ROMP is a convenient method to control molecular weight and introduce chemical functionalities.[18–21] Previously, *d*-limonene, a monoterpene, was reported as a chain transfer agent for ROMP.[22] In an ongoing effort to integrate renewable resources with catalytic polymerization methods,[23] this article describes the hyperbranched polymerization of dicyclopentadiene (DCPD) in β-pinene, limonene oxide, and *d*-limonene as a convenient method to provide functional materials with controllable molecular weight and a high degree of branching.

DCPD is a readily available monomer that contains a highly strained norbornene (NB) alkene and a less strained cyclopentene (CP) alkene. ROMP of DCPD with titanium,[24,25] tungsten,[26,27] and ruthenium[28] initiators usually yield linear polymers if the initiator only reacts with the norbornene alkene or insoluble cross-linked networks if the initiator ring opens both alkenes. Controlling the polymerization rate of DCPD with first- and second-generation ruthenium initiators is difficult and produces incomplete conversion and microencapsulation of the initiator molecules by the growing insoluble polymer network.[29]

Experimental Section

Materials. Limonene oxide (97%, Acros), *d*-limonene (97%, Acros), (1*S*)-(−)-β-pinene (99%, Aldrich), toluene (extra dry, Acros), and norbornene (99%, Aldrich) were degassed and purged with nitrogen. Di-*tert*-butyl-hydroxytoluene (BHT) (99%, Acros) was used as received. The second-generation ruthenium complex [(1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride] (Aldrich, Anal. Calcd: C, 65.08; N, 3.30. Found: C, 65.00; N, 3.29) was used as an initiator. Dicyclopentadiene (95%, Acros) was filtered through a plug of alumina and degassed. All polymerizations were assembled in a nitrogen glovebox. Nitrogen (99.995%, high purity grade) was used as received.

Characterization. The ^{1}H and ^{13}C NMR spectra were measured at ambient temperature with a Bruker Avance 300, 600, or 700 MHz NMR in $CDCl_3$ (99.8% D, Cambridge Isotope Laboratories). GC/MS samples were dissolved in acetone and analyzed with an Agilent chromatograph equipped with a mass spectrometer. The molecular weights were measured by gel permeation chromatography (GPC). The GPC system was equipped with a three-angle Wyatt MiniDawn light scattering detector ($\lambda = 690$ nm, 30 mW Ga–As laser), a Wyatt ViscoStar viscometer, and a Waters 410 differential refractometer. The light scattering detector was calibrated with the known Rayleigh ratio for toluene. The specific refractive increments (d*n*/d*c*) were calculated with Wyatt Technology's Astra V software assuming 100% mass recovery. Three columns were heated at 35 °C and eluted with tetrahydrofuran (1.0 mL/min). The columns (MZ SDplus, 5 μm linear, 300 mm × 8 mm) contained 5 μm particles with pore sizes ranging from 50 to 10^6 Å. Polymers solutions (200 μL) in tetrahydrofuran (THF) were injected at a concentration of 5–10 mg/mL.

Thermal analysis was measured with a TA Instruments Q20 differential scanning calorimeter (DSC). The instrument was calibrated according to ASTM E967-03 (standard test method for temperature calibration of differential scanning calorimeters and differential thermal analyzers) and ASTM E968-02 (standard test method for heat flow calibration of differential scanning calorimeters) using a certified indium reference material. After calibration, an indium standard was within the tolerance for melting point (156.61 ± 0.02 °C) and enthalpy of fusion (28.71 ± 0.08 J/g) data provided by TA Instruments. Polymer samples (2–4 mg) were crimped in aluminum pans and measured under a flow of nitrogen (50 mL/min) using a heating rate of 10 °C/min. The reported T_g

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Table 1. Polymerization of Dicyclopentadiene and Norbornene with Monoterpenes[a]

								MHS values[d]	
entry	monomer[b]	solvent	[monomer]/[initiator]	yield (%)	M_w (g/mol)[c]	M_w/M_n[c]	[η] (mL/g)[d]	*a*	*K* (mL/g)
1	DCPD	*d*-limonene	200	90	6260	2.0	6.9	0.43	0.187
2	DCPD	*d*-limonene	1000	93	7570	2.1	7.9	0.54	0.0696
3	DCPD	*d*-limonene[e]	1000	98	54400	2.4	24.4	0.56	0.0628
4	DCPD	limonene oxide	200	98	4580	1.3	5.2	0.36	0.253
5	DCPD	limonene oxide[e]	1000	70	26600	1.5	15.5	0.59	0.0417
6	DCPD	β-pinene	200	99	2120	1.3	3.3	0.44	0.119
7	DCPD	β-pinene	1000	99	2440	1.2	3.5	0.48	0.102
8	DCPD	β-pinene[e]	1000	78	14700	1.4	10.5	0.57	0.0418
9	NB	toluene	1000	98	128000	1.3	118.4	0.64	0.0701
10	NB	*d*-limonene	1000	93	13600	2.1	19.1	0.59	0.0739
11	NB	limonene oxide[e]	1000	90	7870	1.6	18.2	0.69	0.0412
12	NB	β-pinene	1000	99	4220	1.4	9.2	0.72	0.0242

[a] Polymerization conditions: monomer (1.0 mmol), second-generation ruthenium initiator, and monoterpene (3.0 mL) were reacted under nitrogen for 1 h at 50 °C. [b] DCPD = dicyclopentadiene; NB = norbornene. [c] Weight-average (M_w) molecular weights and molecular weight distributions (M_w/M_n) were calculated by gel permeation chromatography (GPC) using light scattering in tetrahydrofuran (THF). [d] Mark−Houwink−Sakarada (MHS) values and intrinsic viscosity ([η]) were measured in THF at 35 °C using a GPC system with light scattering and viscometer detectors. [e] Polymerizations were run with monomer (1.0 mmol), toluene (3.0 mL), and monoterpene ([monomer]/[monoterpene] = 5) for 1 h at 50 °C.

values were taken as the midpoint of the transition from the second heating cycle.

General Method for Polymerizations with Neat Monoterpenes. The second-generation ruthenium initiator ([monomer]/[initiator] = 200−1000) was stirred in a monoterpene solvent (2.0 mL) until the initiator dissolved. Then, the initiator solution was added to a vial containing monomer (1.0 mmol) and monoterpene (1.0 mL). After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into a methanol (125 mL) containing BHT, stirred, recovered, and dried under vacuum.

General Method for Polymerizations with Stoichiometric Amounts of Monoterpenes. Monomer (1.0 mmol) and monoterpene ([monomer]/[monoterpene] = 5−40) were added to a vial with toluene (2.0 mL). The second-generation ruthenium initiator ([monomer]/[initiator] = 1000) was dissolved in toluene (1.0 mL). Then, the initiator and monomer solutions were combined. After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into a methanol (125 mL) containing BHT, stirred, recovered, and dried under vacuum.

Polymerization of Dicyclopentadiene in *d*-Limonene (Entry 1, Table 1). The second-generation ruthenium initiator (0.0042 g, 0.0050 mmol) was stirred in *d*-limonene (2.0 mL) until the initiator dissolved. Then, the initiator solution was added to a vial containing dicyclopentadiene (0.132 g, 1.0 mmol) and *d*-limonene (1.0 mL). After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into methanol (125 mL) containing BHT. After stirring, the polymer was recovered and dried under vacuum (0.119 g, 90% yield). GPC (in THF): M_w = 6260 g/mol, M_w/M_n = 2.0, [η] = 6.9 mL/g. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.95−5.75 (m, 0.74 H, vinyl and allyl alkene C*H*), 5.66 (br, 4.5 H, cyclopentene alkene C*H*), 5.6−5.15 (m, 12.7 H, *cis/trans* alkene C*H*), 5.15−5.05 (br, 0.43 H, trisubstituted alkene C*H*), 5.05−4.86 (br, 1.0 H, alkene C*H*$_2$), 4.8−4.6 (m, 0.55 H, alkene C*H*$_2$), 3.23 (br, 4.7 H, C*H*), 2.84 (m, 8.0 H, C*H*), 2.59 (m, 4.6 H, C*H*), 2.24 (m, 8.0 H, C*H*$_2$), 2.0 (br, 1.3 H, C*H*$_2$), 1.58 (m, 5.6 H, C*H*$_2$) and 1.23 (m, 3.4 H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 142.33 (vinyl *C*H), 140.49 (vinyl *C*H), 140.17 (vinyl *C*H), 140.05 (vinyl *C*H), 132.56 (alkene *C*H), 131.47 (alkene *C*H), 130.80 (alkene *C*H), 114.39 (vinyl *C*H$_2$), 114.30 (vinyl *C*H$_2$), 113.73 (vinyl *C*H$_2$), 113.64 (vinyl *C*H$_2$), 109.04 (alkene *C*H$_2$), 55.48 (*C*H), 55.26 (*C*H), 55.00 (*C*H), 54.69 (*C*H), 48.03 (*C*H), 47.20 (*C*H), 47.11 (*C*H), 47.00 (*C*H), 46.89 (*C*H), 46.81 (*C*H), 46.19 (*C*H), 46.14 (*C*H), 46.02 (*C*H), 45.91 (*C*H), 45.80 (*C*H), 45.31 (*C*H), 45.18 (*C*H), 45.12 (*C*H), 44.30 (*C*H), 44.19 (*C*H), 44.09 (*C*H), 43.85 (*C*H), 43.71 (*C*H), 42.35 (*C*H), 42.16 (*C*H), 41.97 (*C*H), 41.59 (*C*H), 41.47 (*C*H), 41.38 (*C*H), 41.32 (*C*H), 41.16 (*C*H), 38.70 (*C*H$_2$), 37.82 (*C*H$_2$), 36.60 (*C*H$_2$), 36.55 (*C*H$_2$), 35.66 (*C*H$_2$), 35.58 (*C*H$_2$), 35.47 (*C*H$_2$), 34.95 (*C*H$_2$), 34.91 (*C*H$_2$), 34.84 (*C*H$_2$), 34.69 (*C*H$_2$), 34.63 (*C*H$_2$), 25.81 (*C*H$_3$), and 23.14 (*C*H$_3$) ppm.

Polymerization of Dicyclopentadiene with Limonene Oxide (Entry 5, Table 1). Dicyclopentadiene (0.132 g, 1.0 mmol) and limonene oxide (0.030 g, [DCPD]/[limonene oxide] = 5) was added to a vial containing toluene (2.0 mL). Then, a stock solution of second-generation ruthenium initiator (0.000 85 g, 0.0010 mmol) in toluene (1.0 mL) was added. After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into methanol (125 mL) containing BHT, stirred for several hours, filtered, and dried under vacuum (0.092 g, 70% yield). GPC (in THF): M_w = 26 600 g/mol, M_w/M_n = 1.5, [η] = 15.5 mL/g. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.95−5.75 (m, 1.14 H, vinyl and allyl alkene C*H*), 5.66 (br, 15.0 H, cyclopentene alkene C*H*), 5.6−5.15 (m, 47.2 H, *cis/trans* alkene C*H*), 5.15−5.05 (br, 1.04 H, trisubstituted alkene C*H*), 5.05−4.86 (br, 1.0 H, alkene C*H*$_2$), 4.8−4.6 (m, 1.15 H, alkene C*H*$_2$), 3.23 (br, 16.0 H, C*H*), 2.84 (m, 30.3 H, C*H*), 2.59 (m, 18.8 H, C*H*), 2.24 (m, 33.1 H, C*H*$_2$), 2.0 (br, 3.4 H, C*H*$_2$), 1.58 (m, 20.1 H, C*H*$_2$) and 1.23 (m, 18.4 H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 140.59 (vinyl *C*H), 140.25 (vinyl *C*H), 140.11 (vinyl *C*H), 135.85 (alkene *C*H), 135.20 (alkene *C*H), 132.67 (alkene *C*H), 132.53 (alkene *C*H), 131.51 (alkene *C*H), 130.98 (alkene *C*H), 130.86 (alkene *C*H), 130.75 (alkene *C*H), 114.32 (vinyl *C*H$_2$), 113.81 (vinyl *C*H$_2$), 113.67 (vinyl *C*H$_2$), 109.82 (alkene *C*H$_2$), 59.60 (epoxide *C*), 57.58 (epoxide *C*), 55.53 (*C*H), 55.27 (*C*H), 55.02 (*C*H), 50.34 (*C*H), 47.26 (*C*H), 47.11 (*C*H), 46.94 (*C*H), 46.20 (*C*H), 46.07 (*C*H), 45.97 (*C*H), 45.86 (*C*H), 45.27 (*C*H), 44.37 (*C*H), 44.21 (*C*H), 44.10 (*C*H), 42.41 (*C*H), 42.23 (*C*H), 42.02 (*C*H), 41.66 (*C*H), 41.53 (*C*H), 41.36 (*C*H), 41.23 (*C*H), 38.72 (*C*H$_2$), 37.87 (*C*H$_2$), 36.64 (*C*H$_2$), 35.70 (*C*H$_2$), 35.61 (*C*H$_2$), 34.99 (*C*H$_2$), 34.70 (*C*H$_2$), 34.30 (*C*H$_2$), 23.20 (*C*H$_3$), and 21.47 (*C*H$_3$) ppm.

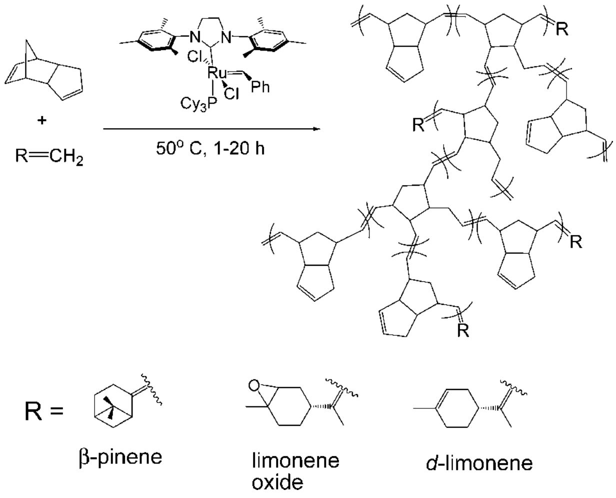
Polymerization of Dicyclopentadiene with β-Pinene (Entry 8, Table 1). Dicyclopentadiene (0.132 g, 1.0 mmol) and β-pinene (0.0272 g, 0.20 mmol, [DCPD]/[β-pinene] = 5) was added to a vial containing toluene (2.0 mL). Then, a stock solution of second-generation ruthenium initiator (0.000 85 g, 0.0010 mmol) in toluene (1.0 mL) was added. After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into methanol (125 mL) containing BHT. After stirring, the polymer was recovered and dried under vacuum (0.131 g, 99% yield). GPC (in THF): M_w = 14 700 g/mol, M_w/M_n = 1.4, [η] = 10.5 mL/g. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.95−5.75 (m, 0.53 H, vinyl and allyl alkene C*H*), 5.66 (br, 6.4 H, cyclopentene alkene C*H*), 5.6−5.15 (m, 21.4 H, *cis/trans* alkene C*H*), 5.15−5.05 (br, 0.76 H, trisubstituted alkene C*H*), 5.05−4.86 (br, 1.0 H, alkene

CH_2), 4.8−4.6 (m, 1.3 H, alkene CH_2), 3.23 (br, 8.0 H, CH), 2.84 (m, 14.7 H, CH), 2.59 (m, 9.5 H, CH), 2.24 (m, 16.7 H, CH_2), 1.94 (br, 2.6 H, CH_2), 1.8 (m, 3.0 H, CH_2) and 1.58 (br, 9.0 H, CH_2), 1.23 (m, 8.6 H, CH_2) and 0.70 (m, 0.88 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 146.07 (vinyl CH), 135.20 (alkene CH), 134.80 (alkene CH), 132.66 (alkene CH), 131.53 (alkene CH), 130.87 (alkene CH), 55.59 (CH), 55.34 (CH), 55.09 (CH), 47.19 (CH), 46.13 (CH), 45.88 (CH), 45.30 (CH), 44.14 (CH), 42.44 (CH), 42.26 (CH), 42.04 (CH), 41.57 (CH), 41.28 (CH), 40.99 (CH), 38.78 (CH_2), 37.95 (CH_2), 36.75 (CH_2), 35.66 (CH_2), 35.01 (CH_2), 34.72 (CH_2), and 34.36 (CH_2) ppm.

Polymerization of Norbornene with Limonene Oxide (Entry 11, Table 1). Norbornene (0.094 g, 1.0 mmol) and limonene oxide (0.030 g, [NB]/[limonene oxide] = 5) were added to a vial containing toluene (1.0 mL). Then, the second-generation ruthenium initiator (0.000 85 g, 0.0010 mmol) was dissolved in toluene (2.0 mL). After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into methanol (125 mL) containing BHT. After stirring, the polymer was recovered and dried under vacuum (0.085 g, 90% yield). GPC (in THF): M_w = 7870 g/mol, M_w/M_n = 1.6, [η] = 18.2 mL/g. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.9−5.7 (m, 0.69 H, vinyl CH), 5.7−5.5 (br, 1.08 H, alkene CH), 5.5−5.25 (m, 43.2 H, *trans*-alkene CH), 5.25−5.1 (m, 21.8 H, *cis*-alkene CH), 5.06−4.8 (m, 2.24 H, alkene CH_2), 2.96 (d, 1.0 H, epoxide CH), 2.9−2.55 (br, 24.1 H, cyclopentane CH adjacent to *cis*-alkene), 2.55−2.2 (br, 48.6 H, cyclopentane CH adjacent to *trans*-alkene), 2.0−1.6 (m, 112.5 H, cyclopentane CH_2), 1.51 (s, 6.5 H), 1.45−1.2 (br, 74.3 H, CH_2) and 1.15−0.85 (m, 35.0 H, cyclopentane bridging CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 143.7 (vinyl CH_2), 143.5 (vinyl CH_2), 138.0 (alkene CH_2), 137.3 (alkene CH_2), 134.16 (alkene CH_2), 134.11 (alkene CH_2), 134.01 (alkene CH_2), 133.94 (alkene CH_2), 133.33 (alkene CH_2), 133.20 (alkene CH_2), 133.04 (alkene CH_2), 129.72 (alkene CH), 129.56 (alkene CH), 129.24 (alkene CH), 128.42 (alkene CH), 125.50 (alkene CH), 112.40 (vinyl CH_2), 59.73 (epoxide C), 57.79 (epoxide C), 51.07 (CH), 44.44 (CH), 43.63 (CH), 43.49 (CH), 43.33 (CH), 42.96 (CH), 42.57 (CH), 42.29 (CH), 41.57 (CH), 40.92 (CH), 38.86 (CH_2), 38.60 (CH_2), 33.27 (CH_2), 33.13 (CH_2), 32.55 (CH_2), 32.39 (CH_2), 31.86 (CH_2), 31.05 (CH_2), 30.04 (CH_2), 24.57 (CH_3), 23.37 (CH_3), 21.69 (CH_3), and 14.07 (CH_3) ppm.

Polymerization of Norbornene in β-Pinene (Entry 12, Table 1). The second-generation ruthenium initiator (0.000 85 g, 0.0010 mmol) was dissolved in β-pinene (2.0 mL). A solution containing norbornene (0.094 g, 1.0 mmol) and β-pinene (1.0 mL) was added. After 1 h at 50 °C, the polymerization was cooled to ambient temperature. The initiator was quenched with ethyl vinyl ether (0.2 mL) in toluene (1 mL). The polymer was precipitated into methanol (125 mL) containing BHT. After stirring, the polymer was recovered and dried under vacuum (0.093 g, 99% yield). GPC (in THF): M_w = 4220 g/mol, M_w/M_n = 1.4, [η] = 9.2 mL/g. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.79 (m, 1.0 H, vinyl CH), 5.39−5.28 (br, 15.5 H, *trans*-alkene CH), 5.27−5.11 (br, 22.9, *cis*-alkene CH), 5.05−5.00 (m, 0.95 H, vinyl CH_2), 4.98−4.92 (dd, 1.17 H, vinyl CH_2), 4.88−4.82 (m, 1.13 H, vinyl CH_2), 2.85−2.69 (br, 23.8 H, cyclopentane CH adjacent to *cis*-alkene), 2.63−2.47 (m, 3.40 H), 2.47−2.35 (br, 16.5 H, cyclopentane CH adjacent to *trans*-alkene), 2.32−2.20 (m, 2.6 H), 2.04 (m, 2.5 H), 1.98−1.91 (m, 2.7 H), 1.91−1.82 (br, 20.4 H, cyclopentane CH_2), 1.82−1.68 (br, 45.8 H, cyclopentane CH_2), 1.39−1.25 (br, 40.6 H, cyclopentane CH_2), 1.24 (br, 3.7), 1.23 (s, 2.4 H), 1.02 (m, 22.8 H, cyclopentane CH_2), 0.82 (m, 2.5 H), 0.70 (s, 2.0 H), and 0.67 (s, 3.1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 152.30 (alkene C), 143.50 (vinyl CH), 143.34 (vinyl CH), 139.92 (CH), 139.85 (CH), 139.75 (CH), 134.12 (CH), 133.99 (CH), 133.83 (CH), 133.78 (CH), 133.17 (CH), 133.03 (CH), 132.88 (CH), 127.20 (CH), 127.11 (CH), 126.99 (CH), 126.98 (CH), 126.79 (CH), 112.36 (CH_2), 112.24 (CH_2), 105.96 (CH_2), 51.75 (CH), 45.53 (CH), 44.54 (CH), 44.27 (CH), 43.47 (CH), 43.37 (CH), 43.28 (CH), 43.23 (CH), 43.15 (CH), 42.78 (CH_2), 42.13 (CH_2), 41.48 (CH_2), 41.37 (CH_2), 41.04 (C), 40.95 (CH), 40.77 (CH_2), 40.68 (C), 40.39 (CH), 38.69 (CH), 38.48 (CH), 38.42 (CH), 38.14 (CH), 33.50 (CH_2), 33.38 (CH_2), 33.10 (CH_2), 32.93 (CH_2), 32.36 (CH_2), 32.22 (CH_2), 31.83 (CH_2), 31.66 (CH_2), 26.97 (CH_2), 26.33 (CH), 26.13 (CH), 26.09 (CH_2), 25.79 (CH), 25.11 (CH_2), 23.98 (CH_2), 23.59 (CH_2), and 21.88 (CH_3) ppm.

Scheme 1. Polymerization of Dicyclopentadiene (DCPD) with Monoterpenes (R = CH_2) Using a Second-Generation Ruthenium Initiator ([DCPD]/[Initiator] = 200−2000)



Results and Discussion

As detailed in Scheme 1 and Table 1, the polymerization of DCPD in the presence of monoterpenes depends on chain transfer and secondary metathesis reactions to prevent insoluble products. Comparing the polymerization in neat monoterpenes with stoichiometric amounts of monoterpenes in toluene indicated both methods resulted in high yields and produced homogeneous, soluble polymers. The weight-average (M_w) molecular weights and intrinsic viscosities ([η]) could be adjusted by choice of monoterpene, the polymerization method, and initiator loading. The M_w values resulting from chain transfer to monoterpenes decreased as follows: *d*-limonene > limonene oxide > β-pinene. Replacing neat *d*-limonene (entry 2) with stoichiometric quantities of *d*-limonene in toluene (entry 3) increased the [η], M_w, and M_w/M_n values. In contrast, increasing the amount of initiator in entry 1 decreased the [η] and M_w values.

Two control experiments were conducted to examine the suitability of commercially available monoterpenes as chain transfer agents. First, the purity of β-pinene (99%) and *d*-limonene (97%) was examined. Naturally occurring β-pinene and *d*-limonene contain approximately 1% and 2% of β-myrcene, respectively. β-Myrcene is a monoterpene (C_{10}) that will undergo metathesis reactions. During ROMP, the ratio of [β-myrcene]/[monomer] is more significant for polymerizations with neat monoterpenes than stoichiometric amounts of monoterpenes in toluene. However, stirring *d*-limonene and β-pinene with a second-generation ruthenium initiator (0.3 mg/mL) at 50 °C for 3 days reduced the quantity of β-myrcene (<0.1%) as detected by GC/MS. This control experiment suggests that a previously prepared stock solution of initiator may be advantageous. Second, the possibility of monoterpene isomerization was examined by NMR and GC/MS. β-Pinene is reported to undergo a thermal ene reaction with formaldehyde at 180 °C to produce an alcohol[30] and a thermally induced cycloreversion reaction to produce β-myrcene.[31] In the presence of a second-generation ruthenium initiator, the mild reactions conditions at 50 °C did not result in detectable amounts of isomerization or cycloreversion by ^{1}H NMR after 24 h.

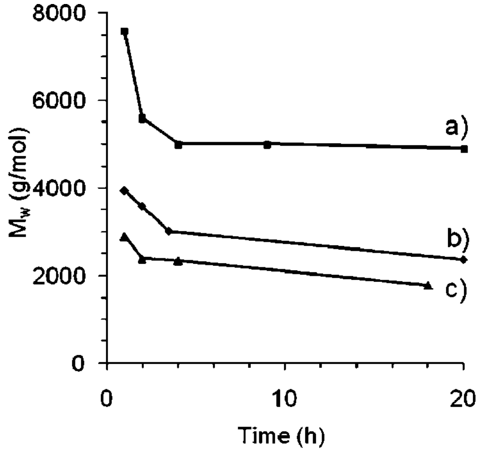


Figure 1. Gel permeation chromatography data (light scattering detector) for ring-opening metathesis polymerizations of dicyclopentadiene (DCPD) at 50 °C with a second-generation ruthenium initiator ([DCPD]/[initiator] = 1000). The polymerizations were run using (a) 0.3 M DCPD in neat *d*-limonene, (b) 0.75 M DCPD in neat *β*-pinene, and (c) 0.3 M DCPD in neat *β*-pinene.

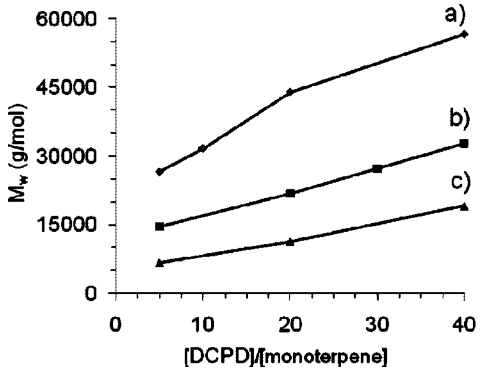


Figure 2. Gel permeation chromatography data (light scattering detector) for ring-opening metathesis polymerizations of dicyclopentadiene (DCPD) at 50 °C with a second-generation ruthenium initiator ([DCPD]/[initiator] = 1000). Stoichiometric amounts of monoterpene in toluene with DCPD (0.3 M) were examined for (a) limonene oxide after 1 h, (b) *β*-pinene after 1 h, and (c) limonene oxide after 24 h.

The M_w values in Figure 1 increased with increasing [DCPD], but the upper [DCPD] limit depended on the monoterpene reactivity. Choosing a monomer concentration of 0.3 M in Table 1 did not result in detectable amounts of insoluble material. In the event of larger [DCPD] values, the rate of chain transfer reactions with *d*-limonene is unable to match the rate of cross-linking reactions.[32] For example, when [DCPD] increased from 0.3 M (Table 1, entry 2) to 0.6 M (M_w = 12 600 g/mol; M_w/M_n = 2.2) and 1.1 M (M_w = 34 200 g/mol; M_w/M_n = 2.8), the propensity for insoluble products increased, and it became difficult to analyze the products by GPC. In contrast, ROMP in *β*-pinene was conducted without solubility problems at 0.75 M. In order to polymerize well-defined hyperbranched polymers, a judicious choice of [DCPD] kept the batch polymerizations homogeneous.

Figures 1 and 2 suggest M_w varies with polymerization time and ratio of [DCPD]/[monoterpene]. The highest M_w values occurred for short polymerization times and high [DCPD]/[monoterpene] ratios. Although typical AB$_n$ hyperbranched polymerizations result in M_w values that increase with increasing time, during ROMP reversible intermolecular and intramolecular reactions are superimposed on cross-metathesis reactions with monoterpenes. The resulting polymers still contain a high degree of branching, but M_w values gradually decrease as a function of time. A similar molecular weight trend was noted for the polymerization of NB in toluene. Even as the M_w values decrease with time, the branching can increase as the less reactive CP units start to ring open.

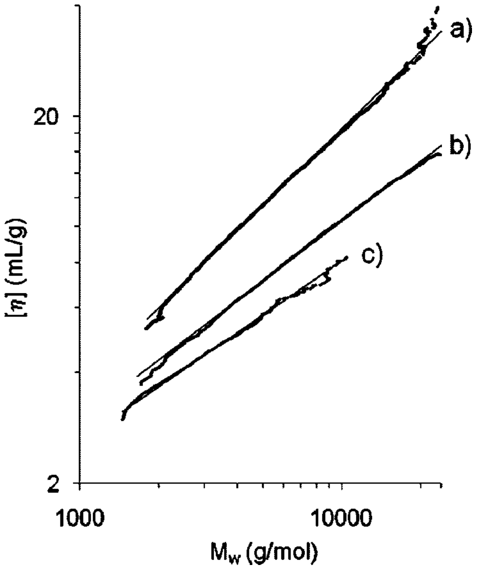


Figure 3. Mark–Houwink–Sakarada plots for ring-opening metathesis polymerizations of (a) norbornene in *β*-pinene (entry 12, Table 1), (b) dicyclopentadiene (DCPD) in *d*-limonene (entry 2, Table 1), and (c) DCPD in *β*-pinene (entry 7, Table 1). The polymerizations were run at 50 °C for 1 h with monomer (0.3 M) and a second-generation ruthenium initiator ([monomer]/[initiator] = 1000).

The second virial coefficients were investigated to determine the solubility and potential aggregation for hyperbranched polymers in tetrahydrofuran (THF). Although certain hyperbranched polymers with polar functional groups aggregate in THF,[33] hydrocarbon polymers with terminal *d*-limonene and *β*-pinene units would not be able to undergo hydrogen bonding. In Table 1, the positive second virial coefficient for entries 2 ($A_2 = 2.5 \times 10^{-3}$ mol mL/g^2) and 3 ($A_2 = 1.2 \times 10^{-3}$ mol mL/g^2) indicate good solubility in THF. For comparison, these A_2 values were larger than polystyrene standards with equivalent molecular weight.[34,35] Since THF is a good solvent for polystyrene, the hyperbranched polymers with larger A_2 values are assumed to be soluble and not aggregated at finite concentrations.

In order to determine the extent of branching, the viscosity profile for Table 1 was investigated using the Mark–Houwink–Sakarada (MHS) equation which is shown in eq 1.

$$[\eta] = KM^a \qquad (1)$$

As shown in Figure 3, graphing the intrinsic viscosities versus M_w values resulted in a linear relationship. The MHS exponent for DCPD polymerizations ranged from 0.36 to 0.59. These values were less than norbornene (NB) (0.3 M) polymerizations with monoterpenes (a = 0.59–0.72). The lower exponent indicates the DCPD polymerizations are producing more compact branched structures. For comparison, polymerization of DCPD (0.3 M) in toluene produced branched structures (a = 0.45), but the M_w value (M_w = 32 500 g/mol) and molecular weight distribution (M_w/M_n = 2.9) were larger than entry 1, and only a small fraction of the polymer was soluble.

Based on the MHS exponents, branching appears more dependent on the amount of initiator and mode of monomer addition rather than polymerization time. For example, decreas-

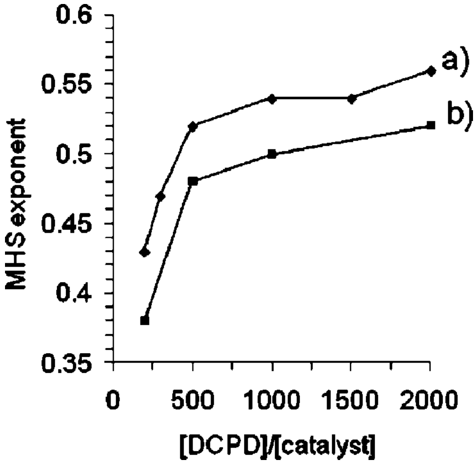
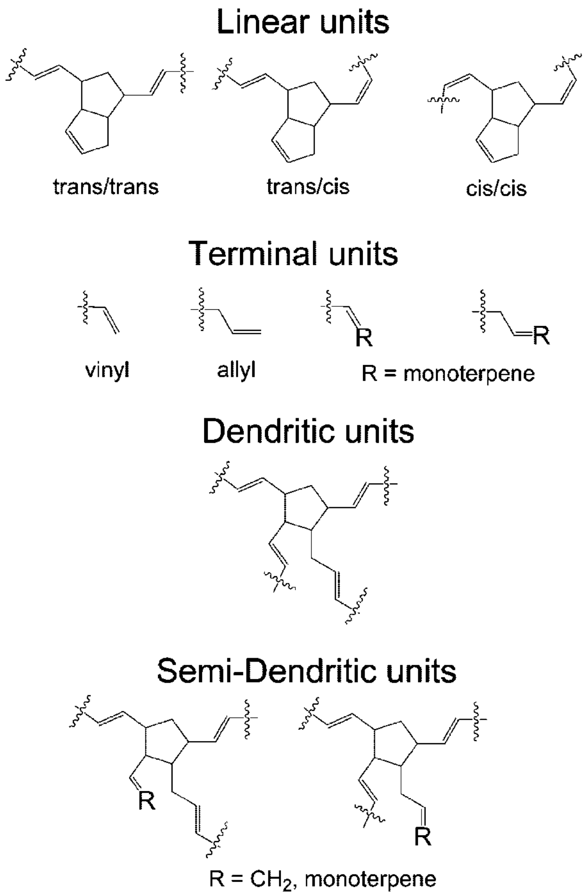


Figure 4. Gel permeation chromatography results for the polymerization of dicyclopentadiene (DCPD). Mark−Houwink−Sakarada (MHS) exponents were measured at 50 °C in *d*-limonene for (a) 1 h and (b) 20 h.

ing the [DCPD]/[initiator] ratios in Figure 4 from 2000 to 200 decreased the *a* value from 0.56 to 0.43. Likewise, incremental monomer addition decreased *a* and increased the branching compared to batch polymerizations. Adding monomer over a 5 h period lowered the MHS exponent from 0.54 (entry 2, Table 1) to 0.39 (M_w = 1920 g/mol; M_w/M_n = 1.2) and presumably allowed a larger fraction of CP rings to ring open. In agreement with other experimental and theoretical studies,[33,36] the gradual addition of monomer also lowered the molecular weight distribution from 2.1 (entry 2, Table 1) to 1.2. For the [DCPD]/[initiator] ratios that were examined in Figure 4, changing the polymerization time from 1 to 20 h had less influence on *a*. Changing these experimental parameters probably increased the fraction of dendritic and semidendritic units (Scheme 2), but cyclization and the formation of intramolecular loops may also play a role in decreasing the MHS exponent and the molecular weight distribution.

Scheme 2. Possible Linear (L), Terminal (T), Dendritic (D), and Semidendritic (sD) Units in Hyperbranched Poly(dicyclopentadiene)



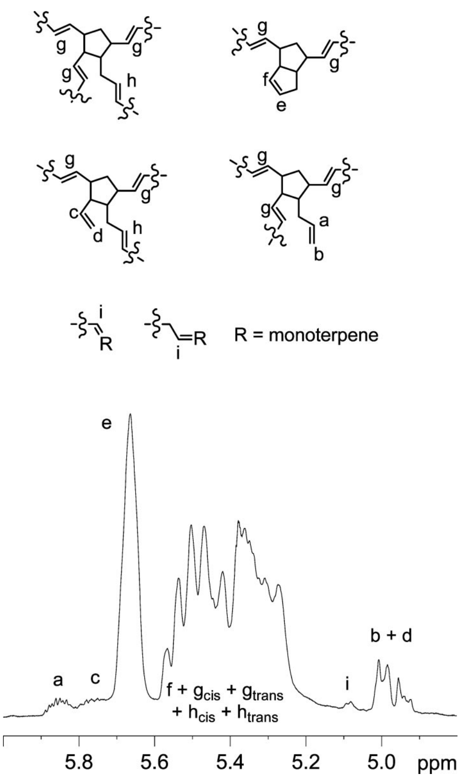


Figure 5. ^{1}H NMR (600 MHz, $CDCl_3$) spectroscopy for ring-opening metathesis polymerizations of dicyclopentadiene (DCPD) in *d*-limonene at 50 °C after 20 h using [DCPD]/[initiator] = 2000 (entry 5, Table 2).

In order to characterize the structure of poly(DCPD), linear (L), terminal (T), dendritic (D), and semidendritic (sD) units in Scheme 2 were characterized by ^{1}H NMR spectroscopy.[37] After the polymerization of DCPD in monoterpenes, ^{1}H NMR spectroscopy in Figure 5 indicated the norbornene C−H alkene resonance (δ 5.95 ppm) disappeared, but the cyclopentene C−H alkene resonance (δ 5.66 ppm) for L units partially remained.[38] ^{1}H NMR analysis also detected *cis*/*trans* disubstituted alkenes (δ 5.6−5.2 ppm) for L and D units. In addition, the C−H resonance for T-vinyl (δ 5.90−5.81 ppm), T-allyl (δ 5.81−5.72 ppm), and T-trisubstituted alkenes (δ 5.15−5.05 ppm) indicated the presence of sD units. In some cases, T units could be confirmed by the saturated region of the NMR spectrum. For example, ^{1}H (δ 2.97 ppm) and ^{13}C (δ 59.7 and 57.8 ppm) NMR spectroscopy detected the epoxide resonance for NB polymerizations with limonene oxide.

Based on ^{1}H NMR integrations for L, T, D, and sD units, the degree of branching (DB) was estimated. It appears that the number of units decreased in the following order: L > sD ∼ T > D.[39] The substantial number of L units is expected to result from the large reactivity difference between NB and CP alkenes that is accentuated by batch polymerizations compared to incremental monomer addition. Although D units in poly(DCPD) more closely resemble an AB_3 system, semidendritic

Table 2. Degree of Branching and Average Number of Chain Ends for Poly(dicyclopentadiene)[a]

entry	solvent	[monomer]/[initiator]	[DCPD]/[monoterpene]	time (h)	X_n[b]	DB[c]	chain ends[d]	monomers/chain end
1	*d*-limonene	200	0.054	1	24	0.40	5.8	4.1
2	*d*-limonene	1000	0.054	1	27	0.36	4.9	5.5
3	*d*-limonene	200	0.054	20	16	0.51	4.5	3.6
4	*d*-limonene	1000	0.054	20	20	0.47	5.0	4.0
5	*d*-limonene	2000	0.054	20	24	0.45	5.4	4.4
6	limonene oxide[e]	1000	5	1	134	0.47	11.0	12.2
7	β-pinene[e]	1000	40	1	146	0.51	9.2	15.9
8	β-pinene[e]	1000	5	1	69	0.60	6.0	11.5

[a] Polymerizations conducted with monomer (1.0 mmol), solvent (3.0 mL), and second-generation ruthenium initiator at 50 °C under nitrogen. [b] Number-average (X_n) degree of polymerization was calculated from gel permeation chromatography (GPC) data (light scattering in tetrahydrofuran). [c] Degree of branching calculated by ^{1}H NMR spectroscopy using DB = (2D + sD)/[(2/3)(3D + 2sD + L)]. [d] Average number of chain ends calculated from GPC and ^{1}H NMR data. [e] Polymerization conducted in toluene with stoichiometric amounts of monoterpenes.

(sD) units are also possible and can be construed as AB_2 units. As a result, DB was calculated with two different equations. Because of the difficulty of distinguishing between terminal groups attached to sD and L units and the possibility of cyclic loops within the hyperbranched polymers, the range of DB values from AB_2 (DB = 0.29−0.40) and AB_3 (DB = 0.36−0.60) equations might be lower than the actual degree of branching and probably contains an understandable amount of experimental error.[36,40] Both equations suggest the branching in poly(DCPD) samples approaches typical AB_2 systems (DB = 0.53−0.66)[6] but probably contains lower branching than AB_3 systems.[41] The results indicate DB increased with initiator loading and ratio of [DCPD]/[monoterpene]. For example, in Figure 2b, DB increased from 0.51 to 0.60 when the [DCPD]/[β-pinene] ratio changed from 40 to 5.

In Table 2, a combination of GPC and ^{1}H NMR data allowed comparison of the average number of chain ends per polymer and DB as a function of polymerization time. For entry 1, the average number of monomer units per polymer chain (X_n) and the average number of chain ends was 24 and 5.8, respectively. Increasing the polymerization time from 1 to 20 h slightly decreased the average number of chain ends from 5.8 to 4.5 but increased DB from 0.40 to 0.51. This indicates that intramolecular cyclization may be competitive with metathesis reactions involving *d*-limonene. However, longer polymerization times facilitate an increase in DB through the ring-opening of CP alkenes.

The T_g values for hyperbranched polymers depend on the number of branch points, molecular weight, chain end polarity, and the quantity of chain ends.[42,43] In Table 1, the trend for T_g values in entries 1 (T_g = 117 °C), 4 (T_g = 105 °C), and 6 (T_g = 63 °C) scaled with the M_w values obtained for polymerizations in *d*-limonene, limonene oxide, and β-pinene, respectively. In Figure 6, our highest T_g value (T_g = 155 °C) for polymerizations with *d*-limonene approached the maximum value (T_g = 160 °C) reported for a fully cured poly(DCPD) network.[44] For comparison, linear regression analysis (R^2 = 0.975) of T_g values in Figure 6 versus 1/M_w gave an extrapolated T_g value of 158 °C at infinite molecular weight. Although the range of M_w values in Figure 6 strongly influenced the T_g values, the batch polymerizations had less influence on the MHS exponents (0.54−0.56). Interestingly, changing the mode of monomer addition from batch polymerizations in neat *d*-limonene to incremental monomer addition over a 4 h period lowered the MHS exponent (a = 0.45), molecular weight (M_w = 3170 g/mol; M_w/M_n = 1.6), and the glass transition value (T_g = 69 °C) compared to entry 2 (Table 1).

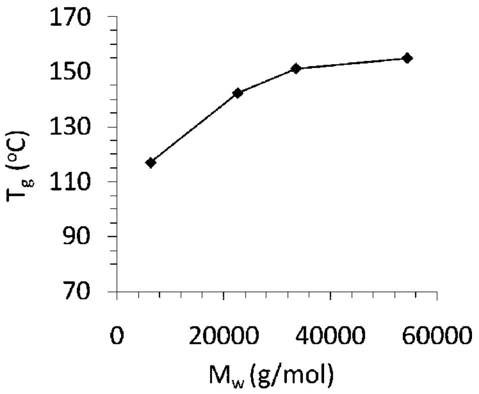


Figure 6. Correlation between glass transition temperatures (T_g) and the M_w values for the batch polymerization of dicyclopentadiene (0.3 M; [DCPD]/[initiator] = 1000) with *d*-limonene at 50 °C after 1 h. The [DCPD]/[*d*-limonene] ratios for the polymerizations ranged from 0.054 to 5. The T_g values were measured by differential scanning calorimetry (10 °C/min), and the M_w values were measured by gel permeation chromatography.

Conclusion

The polymerization of DCPD with monoterpenes provides a one-pot method for functional hyperbranched polymers. This method converts the heterogeneous ROMP of DCPD into a homogeneous polymerization that produces well-defined hyperbranched polymers. During ROMP, chain transfer occurs when a monoterpene alkene reacts with the metathesis initiator. A range of molecular weights and T_g values are available depending on the mode of monomer addition, [monomer], and the choice of monoterpene. As measured by NMR spectroscopy, the degree of branching (DB) varied with polymerization time, initiator loading, and choice of monoterpene.

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Supporting Information Available: GPC, ^{1}H NMR, and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) For AB_3 systems, $DB = (2D + sD)/[(2/3)(3D + 2sD + L)]$; see: Hanselmann, R.; Holter, D.; Frey, H. *Macromolecules* **1998**, *31*, 3790–3801.

(37) The CH_2 and CH protons were assigned based on edited HSQC spectra. Calculations of representative models with *cis*- and *trans*-alkenes in Scheme 2were built using GaussView. The initial structures were optimized using the PM3 semiempirical method, and then they were further optimized using the DFT method at the b3lyp/6-31g** level. The optimized structures were used for the calculation of NMR chemical shifts at the b3lyp/6-311+g(2d,p) level using the GIAO method. All calculations were performed using the G03W program.

(38) The NMR resonance at δ 5.66 ppm represents one of the two cyclopentene alkene C−H bonds. The other cyclopentene alkene C−H resonance overlaps with the resonance for *cis/trans*-disubstituted alkenes (δ 5.6−5.2 ppm).

(39) Further characterization of the overlapping resonances for L and D units is in progress. The resonances for L and D units were resolved with the following equation: $\text{Area}_{\text{D units}} = (\text{Area}_{\delta\ 5.6-5.2}) - 3(\text{Area}_{\delta\ 5.66})$. The sD units were assumed to contain contributions from the vinyl, allyl, and trisubstituted alkene regions according to the following equation: $\text{Area}_{\text{sD units}} \sim (\text{Area}_{\delta\ 5.90-5.81}) + (\text{Area}_{\delta\ 5.81-5.72}) + (\text{Area}_{\delta\ 5.15-5.05})$.

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